Properties of Ionic Bombarded Silicon

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This paper deals with a new and very interesting technique by which the properties of silicon surfaces are altered very materially by bombardment with ions of such gases as hydrogen, helium, nitrogen and argon. The change in rectifying properties has been of special interest but there have been considered also changes in the structural features of the material itself. The effects of bombardment on the rectifying properties are illustrated by a series of characteristic curves systematically arranged to bring out the effects of the several variables of experiment such, for example, as ion velocity, intensity of bombarding current, length of time of bombardment, kind of gas, and the temperature of the specimen during bombardment. The effect of bombardment on materials contaminated with impurities is also illustrated. It is of particular practical importance that silicon contaminated with boron to the point where it shows relatively little rectification can be modified by bombardment to make it even better than most unbombarded materials.

Some years ago, the writer discovered that the electrical properties of silicon surfaces could be greatly modified by bombardment with positive ions. The ions in question were generated in a low pressure discharge in some gas, like hydrogen, helium or nitrogen, and after passing through a perforated cathode were accelerated to a suitable velocity before impinging on the surface to be treated. This scheme may be contrasted with other methods subsequently reported for treating germanium[1] in which high-velocity ions were derived from radioactive sources. Preliminary results of the present research were described in a paper entitled *Silicon Transistors*, by W. J. Pietenpol and the writer, presented at an Electronics Conference held at the University of Michigan, June 22, 1950. Since that time exploration has continued with a view both to learning about basic principles and about possible practical applications.

Editorial Note—Since the resurgence of interest in point-contact rectifiers, considerable research has been carried on into the characteristics of silicon and germanium. The author of this paper was a pioneer in this new field of study, as evidenced, for example, by Patent No. 2,378,944, applied for on July 26, 1939, and Patent No. 2,402,839, applied for on March 27, 1941. More recent work has been described in a large number of text books and technical papers such as *Electrons and Holes in Semi-Conductors* by William Shockley, D. Van Nostrand, 1950, and numerous papers by Lark-Horowitz published mostly in Physical Review. The work described in the accompanying paper is a continuation of this long research.

[1] Brattain and Pearson, *Phys. Rev.*, **80**, Dec. 1950.

The present paper gives the results of some more recent experiments made with improved equipment. Also described briefly are some related experiments in which silicon is bombarded with alpha particles derived from radioactive polonium. The overall results of this work indicate rather clearly that with suitable variations of bombarding voltage, target temperature and time of exposure as well as impurity content in the base material, it is possible to prepare to specification silicon surfaces having a wide range of properties. From the materials so treated it has been possible to construct improved forms of signal rectifiers, harmonic generators, transistors, modulators, gating devices and also photo-electric cells. It is particularly significant that the voltage range over which these newer devices can be operated has been greatly extended, thus making them useful in places not previously regarded as possible. Since these new surfaces appear to be readily reproducible in large numbers and since they are electrically tough, chemically stable and show no unsatisfactory temperature or aging effects, it would appear that bombarding techniques should have considerable practical value.

This paper is concerned mainly with the practical aspect of ion bombardment of silicon, namely its effect on the voltage current characteristics at low frequencies. Equally important, perhaps, are its theoretical aspects, particularly with regard to the interpretation of the rather pronounced changes in the properties in light of presently-accepted views of solid-state physics. These aspects are not covered in this paper.

METHOD

The bombardment process referred to above consists of exposing the silicon surface to ions that have previously been accelerated to energies in the range from about 100 electron volts to about 30 kilo-electron-volts. A recent setup is illustrated in Fig. 1. The electrons from a tungsten cathode are accelerated toward a grid which is at a positive potential with respect to the cathode. Many of the electrons pass a short distance beyond the grid and return for ultimate capture. Ionization due mainly to the impacts of electrons with gas molecules takes place in this turn-around region, producing amongst other things positive particles. Electrodes are so proportioned that this ionization is fairly uniform over the grid area.

The silicon specimen to be bombarded is made negative with respect to the filament. This accelerates the positively charged particles toward the target. The latter rests on a graphite plate heated by a coil below, carrying high-frequency currents. A thermocouple with suitable connections to the exterior makes possible an adequate measurement of

temperature. The apparatus will accommodate circular surfaces as large as $1\frac{1}{2}$ inches diameter. The gases from which ions are derived are admitted through the gas inlet. Thus far experiments have been made with hydrogen, belium, nitrogen and argon. The bombarding voltages have as already noted, been varied from 100 to 30,000 volts and the surface temperatures have been varied from about 20°C to 400°C. The effects of these several variables will be discussed more fully below.

SAMPLE PREPARATION

The material to be bombarded is usually prepared in batches of about 300 grams in fused silica crucibles roughly cylindrieal in shape.[2] After solidifying, the cast is ground to a cylinder approximately $1\frac{1}{2}$ inches

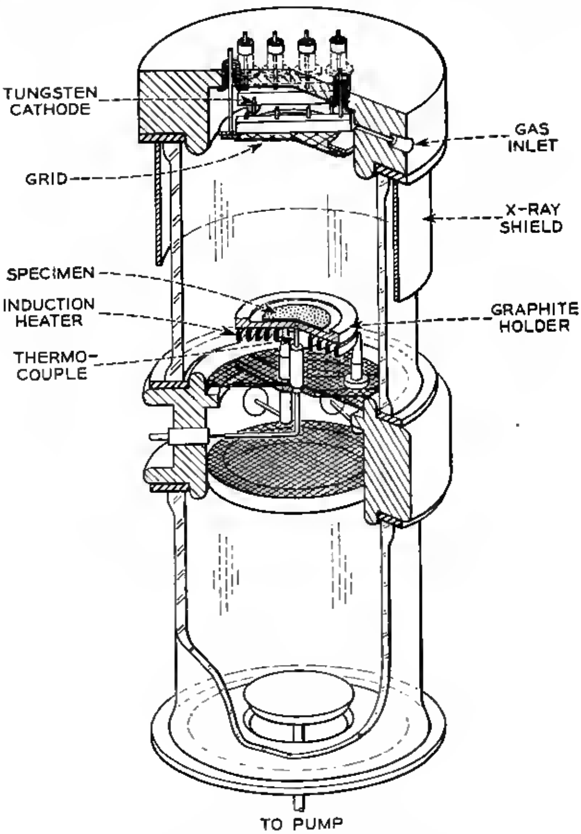


Fig. 1—Bombardment apparatus.

[2] Scaff, Theuerer, and Schumacher, A.I.M.M.E., **185**, pp. 382–392, 1949.

diameter. This has the effect of removing some of the contaminating impurities derived from the crucible as well as providing samples of convenient size. This $1\frac{1}{2}$-inch cylinder is then sliced transversely into thin wafers which subsequently are polished on one side. Except as otherwise noted the material covered by this paper had an impurity content of about 0.1 per cent. The exception will be found in the data of column (a) of Fig. 8.

BOMBARDMENT PROCEDURE

The wafer, as prepared above, is placed in the bombarding apparatus with the rough face contacting the graphite support. The vacuum chamber is sealed by placing the ion generator in position and the whole assembly is evacuated. The sample is then heated to the proper temperature and the desired kind of gas is admitted, the pressure being estimated from the ion current. When stable conditions prevail, the accelerating voltage is applied to the target and the bombardment is carried out for the proper length of time. A convenient current density is 5 microamperes per square centimeter of target area. The target area of our present apparatus, including the silicon and a portion of the graphite support, being 20 square centimeters, the ion current is generally around 100 microamperes. The dosage is sometimes specified in microcoulombs.

After bombardment, the sample is removed from the apparatus and the rough surface is covered with a thin layer of evaporated rhodium. For most of the tests outlined below the $1\frac{1}{2}$-inch diameter wafers were cut into $\frac{1}{8}$-inch squares, a size convenient for testing.

GRAPHICAL REPRESENTATION

In considering the merits of non-linear materials such as silicon, perhaps the simplest and most useful characteristic is the voltage-current relation. If this is plotted to a linear scale, it results in a smooth curve of the general form shown in Fig. 2a. Specific curves obtained in practice may depart widely from that shown but in general, all may be regarded as made up of two semiparabolas, one in the first quadrant and one in the third, joined by a nearly horizontal straight line. For present purposes, we shall further simplify this idealized characteristic by considering it as made up of three straight lines. The first, AB, is associated with the reverse voltage current characteristic. The third, CD, is associated with the forward voltage current characteristic. These two characteristics are joined by the nearly horizontal line, BC. The slopes of these three lines correspond to resistances. The section BC for example, corre-

sponds to a region in which resistance is very high. The points B and C are particularly important for they represent points of inflection where the resistance undergoes rapid change and the material is departing most markedly from Ohm's Law. Ideally they should be sharp but in practice there is usually considerable curvature. Though either inflection point could presumably be used in detection processes, the point to the right of the origin is for practical reasons, usually preferred. Point B defines a voltage E_B at which substantial backward currents flow. It is referred to simply as the *reverse voltage*. In a similar way, point C defines a *forward voltage* E_F. The distance between B and C $(E_B + E_F)$ will be referred to as the *inflection interval*. The difference in these quantities $(E_B - E_F)$ is also of interest. One-half of this voltage difference is referred to as the *self-biasing voltage*. It is a significant quantity readily measured in practice by noting the d-c voltage across a large condenser placed in series with the crystal and a supply of 60 cycles AC. For detectors, point C should preferably be close to the origin and E_F should

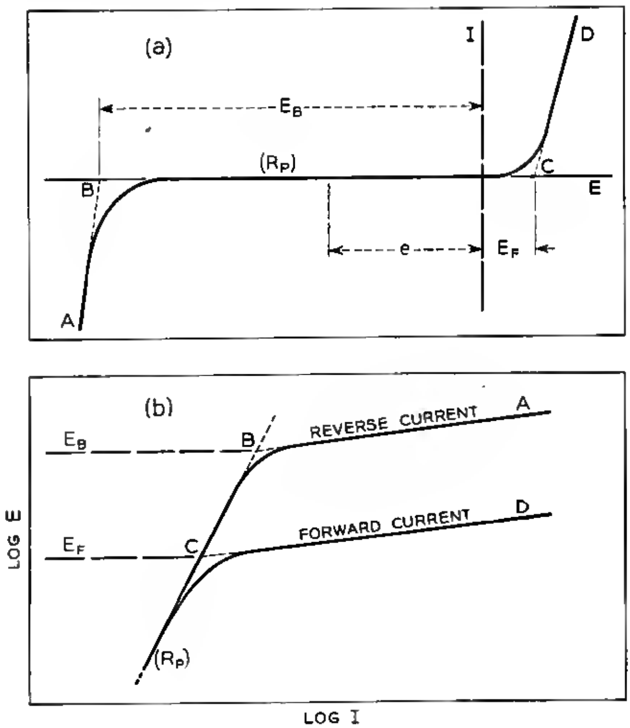


Fig. 2—Idealized characteristic curves.

be small. For certain kinds of voltage limiters, E_F should be large. In either case the inflection interval should be large.

In an alternate graphical representation, see Fig. 2b, voltage-current data are plotted to a log-log scale. This form of representation is of particular value when large ranges of data are to be shown. It is also of value in determining the resistance (R_p) at small voltages. Corresponding points on the two curves shown in Fig. 2 are identifiable by the letters A B, C, and D. Curves of both kinds are used interchangeably to show the effects of the several variables of the experiment.

EFFECT OF CONTACT PRESSURE

In point contact rectifiers,[3] pressure is of considerable importance. Usually the best pressure is a compromise between good electrical characteristics, usually obtainable only with light pressures, and good stability usually obtainable with higher pressures. Experiments have been performed with a range of contact pressures both on bombarded and unbombarded materials. In general, the results are highly variable, particularly in the case of unbombarded material. From this wide range of data, however, two characteristics have been selected that may be regarded as typical for 10-gram and 60-gram pressure. They are shown in Fig. 3 for silicon taken from nearby portions of the same sample. Significant points on these several curves may be compared with their idealized counterparts shown in Fig. 2. Although the samples chosen show somewhat more than the usual intrinsic resistance typical of p-type silicon, the effects of contact pressure are nevertheless regarded as representative. As indicated in Figs. 3a and 3b, the effect of increased contact pressure,[4] particularly in the case of unbombarded material, is of reducing the low voltage resistance, R_p, see Fig. 2b. The more desirable higher resistance is obtainable only with light contact, a condition unfavorable for high mechanical stability. In the case of bombarded material, the effect of contact pressure is less important. Thus it is possible in this case to incorporate in the design higher contact pressures and obtain thereby higher stabilities. For purposes of this paper a contact force of 10 grams has been accepted as standard.

In addition to showing the effect of contact pressure, Fig. 3 shows some overall effects of bombardment. It will be noted, for example, that the effect of bombardment, see Fig. 3b, has been that of shifting the plots of Fig. 3a to the left by several orders of magnitude. Thus the resistance (R_p) is increased by a factor of more than 10,000. It is to be noted also

[3] Scaff and Ohl, *Bell System Tech. J.*, **26**, Jan. 1947.

[4] Realy contact force.

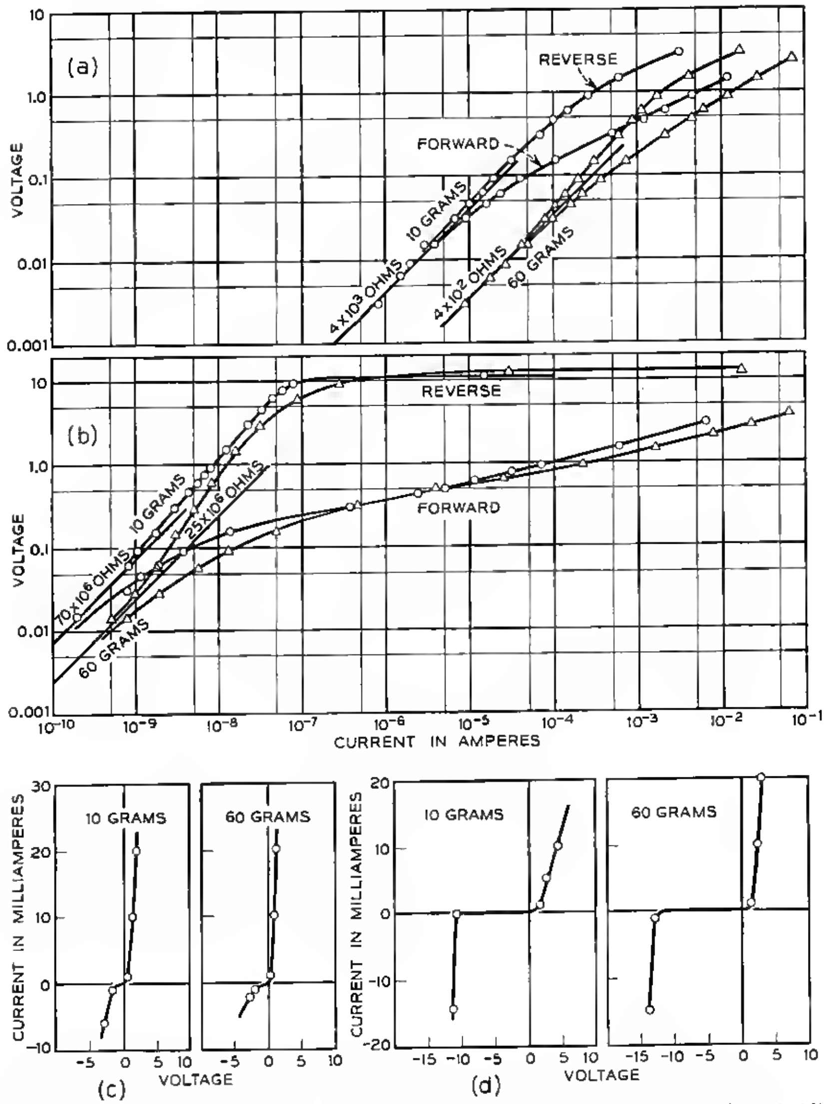


Fig. 3—Characteristic curves. (a) and (c) unbombarded silicon, (b) and (d) silicon bombarded with 30-kv helium ions.

from a comparison of Fig. 3a with Fig. 3b that at the one volt level, the ratio of forward to reverse currents for the unbombarded case is about twenty, whereas that for the bombarded case, is more than 10,000. At other levels the difference is even greater. Referring particularly to Figs. 3c and 3d, it will be seen that one effect of bombardment is that of separating the two significant points of inflection B and C. That is, the inflection interval has been notably increased. This increase is the result of a small increase in the forward voltage and a very substantial increase in the reverse voltage.

EFFECT OF TYPE OF GAS

Four high purity gases were tested as ion sources, namely, hydrogen, helium, nitrogen and argon, having atomic weights respectively of 1, 4,

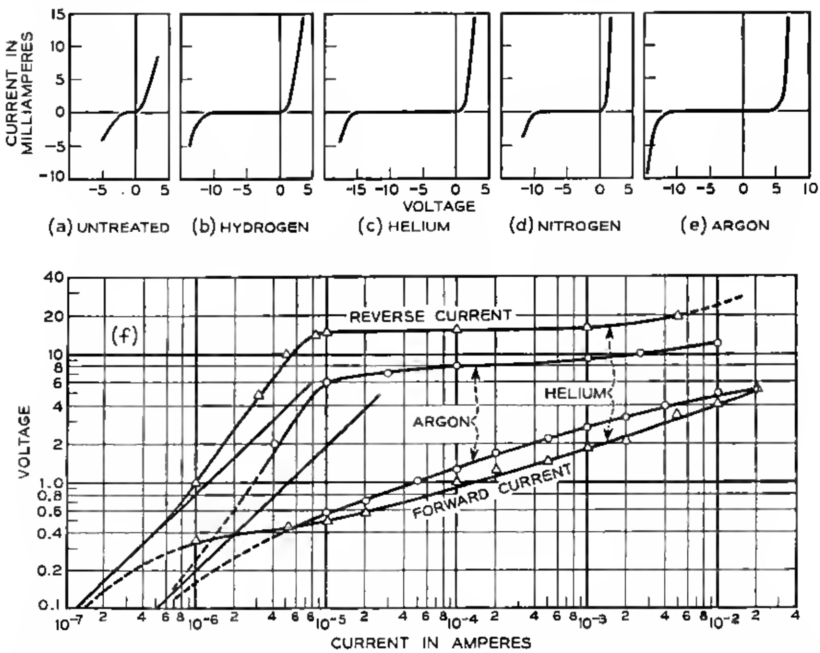


Fig. 4—Characteristics showing effect of various gases all with a bombarding potential of 30 kv.

14 and 40. While all four gases worked very well, helium was the easiest to handle. In the course of the tests, identically prepared samples each $\frac{1}{8}$-inch square, taken from a high-purity silicon melt, were bombarded with ions formed in the particular gas under test. Particular conditions known to be good for producing good rectifier units were adopted as standard for these tests. They corresponded to a total bombarding charge of 600 microcoulombs per sq. cm., a surface temperature of 395°C a contact force of about 10 grams and a bombarding potential of 30 kv.

That the effect of bombardment varies with different gases is seen at a glance from the characteristic current-voltage curves shown in Fig. 4. Figs. 4b to 4e in particular indicate that as compared with an untreated sample, Fig. 4a, the effect of bombardment is in general that already noted of separating the two significant points of inflection, B and C. A rather substantial increase in the forward voltage appears in the case of argon as compared with hydrogen, helium and nitrogen. In contrast with a small increase in the forward voltage resulting from the bombardment of helium, there is a very substantial increase in the backward voltage. Though substantial for all four gases, the effect of bombardment is largest for helium with progressively smaller effects noted respectively for argon, hydrogen and nitrogen. A particular characteristic of helium bombardment, as compared with argon, not readily appreciated from a linear scale, is shown in Fig. 4f. It will be noted that at the one volt level, the ratio of forward to reverse current for helium is about 130 whereas for argon it is about 25. At other levels the difference is even greater. At the moment helium is regarded as a preferred source of ions.

The log-log current-voltage curves show as before that the lowest voltage at which substantial forward currents flow occurs in helium, while the highest forward voltages occur for argon. In a similar way the voltages for substantial reverse currents are highest for helium and lowest for argon. The sharp break in the reverse current characteristic, evident in these cases, has been observed so generally that it is now accepted as typical of bombarded surfaces.

EFFECTS OF TEMPERATURE

Investigations have been made of the properties of silicon surfaces as affected by the temperature at which bombardment was carried out. This has been done not only for surfaces used as rectifiers but surfaces used as transistors and as photo-electric cells as well. In the case of rectifiers, a procedure was adopted similar to that used in the previous tests. Measurements were made at five different temperatures ranging from

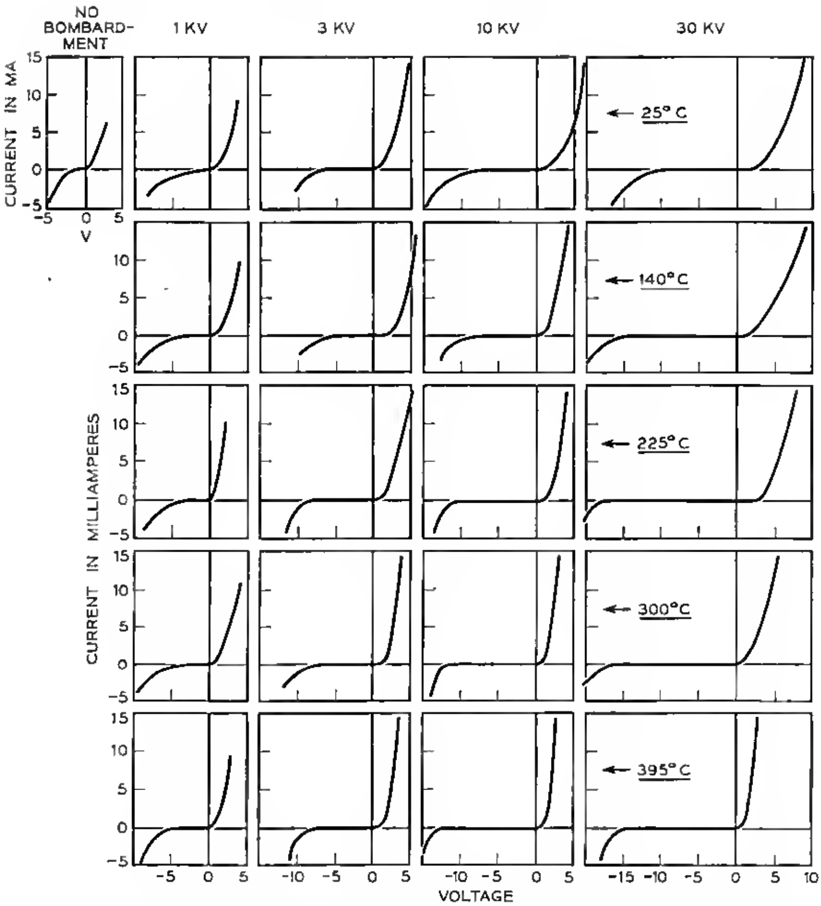


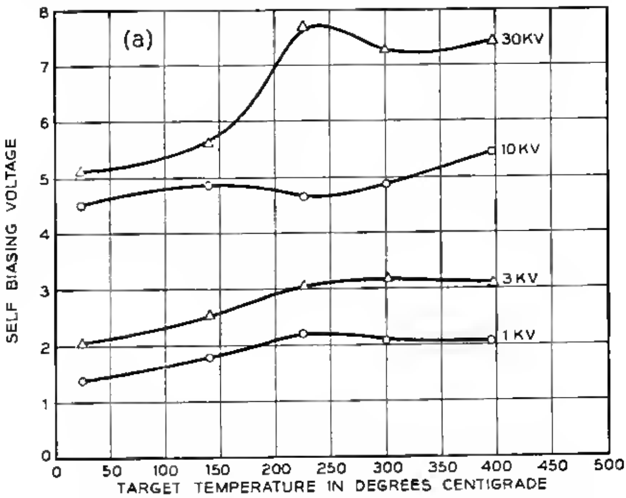
Fig. 5—Characteristics showing effects of voltage and temperature variation.

25°C to 395°C each at accelerating voltages of 1 kv, 3 kv, 10 kv and 30 kv using helium gas. The data so obtained were useful not only for studying the effect of temperature but useful in the studies of the effect of ion velocity as well. The latter will be discussed in the following section.

The results of the above measurements are plotted in Fig. 5. They are further summarized in Fig. 6a. The latter figure, in particular, indicates that as rectifiers, there is little choice of surface temperature between about 250°C and 400°C. It has been found, however, that for temperatures below about 250°C the point contact seems to be more vulnerable to electrical shock.

EFFECT OF ION VELOCITY

The effect of ion velocity (bombarding voltage) has been investigated for several types of silicon. The effects vary with the different types. Typical results are those given in Fig. 5 already referred to. It will be noted from a comparison of the data for a particular temperature, say 300°C, that the principal effect of increased ion velocity is that of increasing the reverse voltage. Values of these reverse voltages E_B and also the



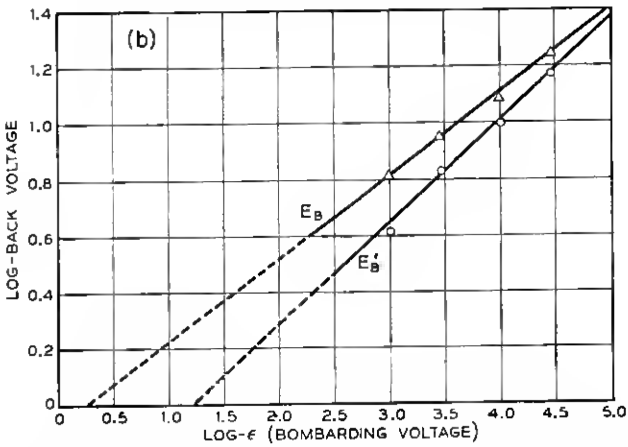


Fig. 6—Summary of data of Fig. 5. (a) effect of temperature and bombarding voltage on self biasing voltage; (b) effect of bombarding voltage on reverse voltage.

TABLE I—EFFECT OF BOMBARDMENT VOLTAGE ON E_B AND E_F

Surface Temp. Deg. C.	30 KV		10 KV		3 KV		1 KV		No Bombardment	
	E_B	E_F	E_B	E_F	E_B	E_F	E_B	E_F	E_B	E_F
395	16.7	1.3	14.0	1.5	10.0	1.5	7.1	1.0		
300	16.5	1.5	12.5	1.2	10.0	2.0	6.5	1.0		
225	18.5	3.6	12.5	1.5	9.6	1.5	5.5	0.3		
140	17.5	2.5	9.8	1.5	6.7	2.5	7.0	1.2		
Mean	17.3	2.0	12.1	1.4	9.1	1.9	6.5	0.9	2.4	0.5
Mean E'_B	14.9		9.7		6.7		4.1			

corresponding forward voltages E_F have been scaled from the above drawings and have been tabulated below. Since they vary only slightly with surface temperature, only their mean values are regarded as significant. Mean values of E_B are plotted in Fig. 6b.

In order to isolate further the effects of bombardment we bave subtracted from tbe mean values of E_B value of E_B for untreated silicon. Thus tbe curve marked E'_B represents the improvement in backward voltage that has accrued from bombardment alone. This is also tabulated as the mean E'_B in Table I.

EFFECT OF TOTAL CHARGE

Tests have been made to determine the effect of time of bombardment on the rectifying properties of silicon surfaces. In these tests, specimens taken from neighboring regions of the same melt were exposed for progressively longer periods all at tbe same bombarding potential of 30 kv and the same rate and density of application, 5 microamperes per square centimeter. Representative current-voltage characteristics are plotted in Figs. 7a and 7b for two neighboring regions. The results are summarized in Fig. 7c. Tbe latter show a ratber rapid improvement of back voltage E_B with total cbarge up to perhaps 50 microcoulombs per square centimeter.[5] Thereafter the improvement is small. For purposes of comparison, there is plotted as a vertical line a value of bombarding charge that would account theoretically for one positive ion in each unit crystallographic cell on the surface layer. This suggests that when all surface cells have been penetrated by a single ion, no marked increase in back voltage can be effected.

[5] Specifying results in terms of microcoulombs implies that bombarding effects are independent of the rate of application. This is known to be true only between factor limits of $\frac{1}{2}$ and 2 of the bombarding current.

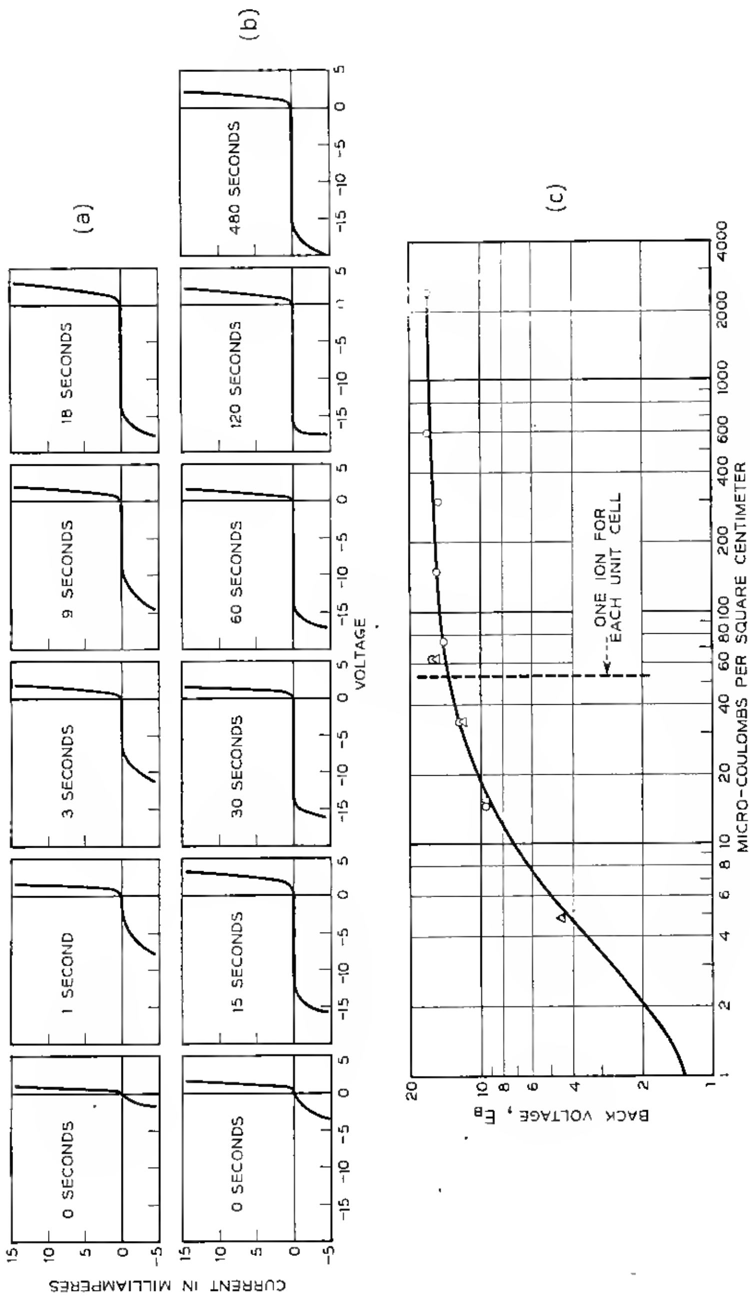


Fig. 7—Effect of time and bombarding charge on back voltage.

EFFECT OF MATERIAL COMPOSITION

Thus far discussions have centered around a single type of high purity material that was regarded as representative. It is of interest to examine the effect on other materials particularly those in which impurities have been added. For this purpose tests were made on comparable samples from four sources all bombarded for two minutes with 5 microamperes of current and each with five representative bombarding voltages. The results are illustrated by the curves shown in Fig. 8. The four columns correspond to progressively higher percentages of impurities beginning with (a) on the left as a material having an impurity content believed to be less than 0.01 per cent. The impurity content of (b) is not known accurately except that it lies between (a) and (c). The material represented by column (c) was produced by adding 0.02 per cent boron[6] to a material illustrated in column (a). The last column (d) was produced by adding 0.1 per cent boron to the material illustrated in column (b).

It is to be noted from Fig. 8 that marked changes in the voltage-current characteristic may be effected by bombardment for all degrees of the impurity content shown. It is especially interesting that in columns (c) and (d) corresponding to materials contaminated with boron to the point where nonlinearity is almost absent, rectification can not only be restored but indeed the product may be made better than the best unbombarded material.

EFFECTS OF ALPHA-PARTICLE BOMBARDMENT

The close relationship between helium ions such as generated above and alpha particles such as emanate from radioactive materials suggests that the latter may be used for the bombardment of silicon surfaces. A few experiments of this kind have been made with results that are not only interesting but possibly useful. For these tests, four sources of alpha particles were obtained. They consisted of $\frac{5}{16}$ inch square pieces of nickel on which had been plated a thin coating of polonium followed by a covering of gold. The initial strength was 4 millicuries per square centimeter. The half-life of polonium is 140 days.

The process of bombardment consisted simply of placing the polished surface of a standard silicon square against the layer of gold and examining the same periodically. Tests of four samples were carried out simultaneously. The results are given in Table II. The data for Sample No. 1 departs so markedly from the mean that it may be disregarded. Since

[6] Boron is a particularly active agent in effecting changes in the properties of silicon.

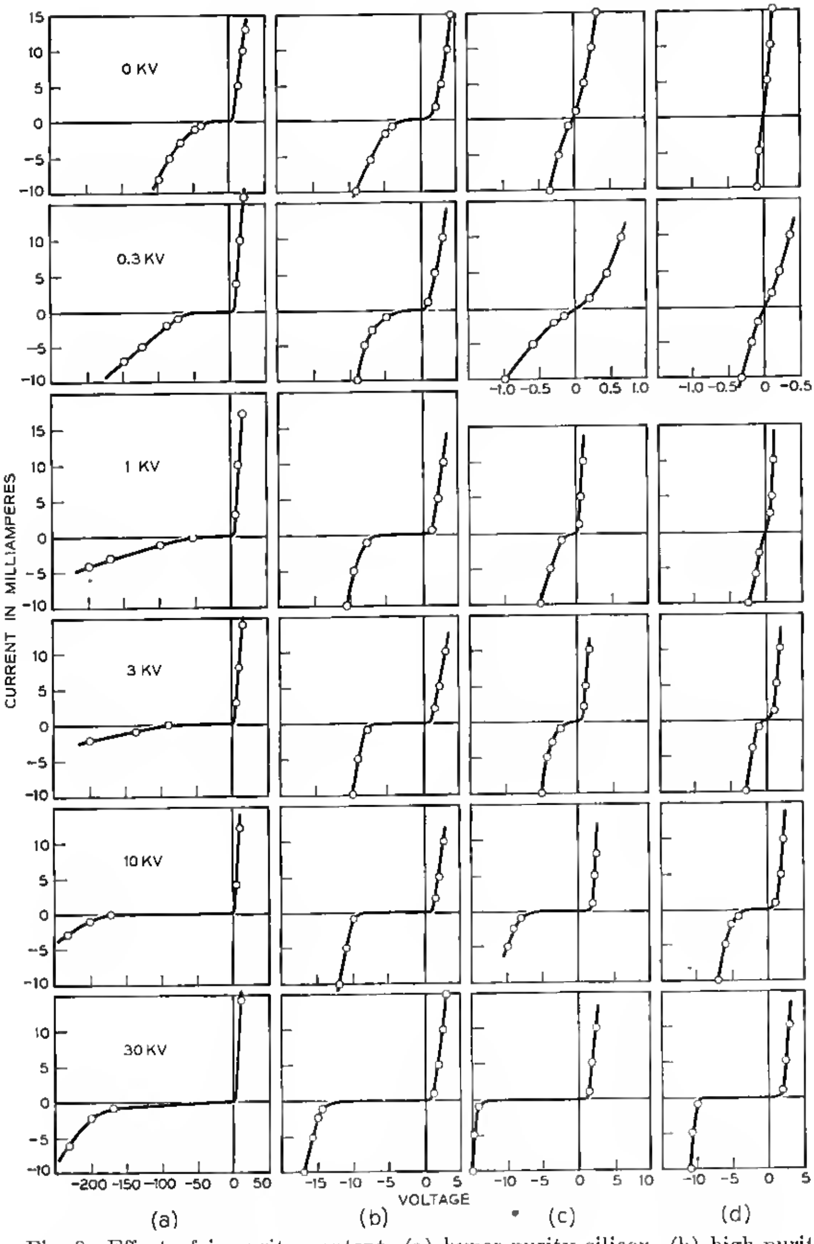


Fig. 8—Effect of impurity content. (a) hyper-purity silicon, (b) high-purity silicon, (c) hyper-purity silicon plus 0.02 per cent boron, (d) high-purity silicon plus 0.1 per cent boron.

the data for self-bias are the result of a direct measurement while those for forward and reverse voltage are transcribed from a cathode-ray plot, they are perhaps the most significant. Samples 1 to 3 represent specimens of increasing degrees of purity.

These alpha-particle bombardment experiments indicate rather definitely that results may be obtained similar to those obtained from bombardment with gaseous ions and, like the ion bombardment, they tend to produce high resistance surfaces.

TABLE II

Days of Exposure		Sample Number			
		1	2	3a	3b
4	Self Bias-Volts	<1	6	180	60
4	Reverse Voltage	<1	20	380	130
4	Forward Voltage	<0.5	<0.5	<1	<1
13	Self Bias-Volts	<1	160	200	190
13	Reverse Voltage	1	360	440	420
13	Forward Voltage	<0.5	<0.5	<1	<1
39	Self Bias-Volts	<1	60	130	100
39	Reverse Voltage	0.5	480	500	500
39	Forward Voltage	<0.2	350	180	180
56	Self Bias-Volts	<1	70	150	110
56	Reverse Voltage	0.5	440	560	560
56	Forward Voltage	0.3	320	320	240
66	Self Bias-Volts			100	85
66	Reverse Voltage			560	520
66	Forward Voltage			200	320

MECHANICAL EFFECTS OF BOMBARDMENT

The marked changes in the electrical properties of silicon imposed by bombardment strongly suggest that bombardment may also impose a corresponding change in the lattice structure and that this might be detected by suitable optical methods. Attempts were made at an early date to detect such changes. To this end a mask of nichrome ribbon 5 mils wide and 1 mil thick was laid over a sample of silicon during bombardment. An optical examination of the surface showed that after bombardment in the case of helium the surface on either side of the mask was elevated whereas in the case of argon it was depressed. This result has since been confirmed by one of the authors's colleagues, Dr. F. W. Reynolds, who has found that in cases of prolonged bombardment by helium the adjacent surfaces may be elevated by as much as 225 Angstroms[7] while in the cases of prolonged bombardment by

[7] One Angstrom is 10^{-8} cm.

argon the adjacent surfaces may be depressed by as much as 130 Angstroms. Further investigation of this phenomenon is under way.

STABILITY OF BOMBARDED SURFACES

No extended test has yet been made of the stability of bombarded surfaces but results extending over more than two years are encouraging. Similarly, rectifiers for the millimeter wavelength range, mounted without the usual protective impregnation, show little or no change at the end of a year.

In a few instances bombarded surfaces have been subjected to rather severe tests with results that suggest that under normal conditions they may be even more stable than surfaces activated by more conventional methods. For example, surfaces contaminated while cutting or while cementing them to their mountings have subsequently been cleaned with solvents such as alcohol and are substantially the same before and after treatment. In other cases, they have been heated in a flame to soldering temperatures with no appreciable effects. Even in the very severe case where the bombarded piece was heated to a cherry red and the superficially oxidized layer was removed with hydrofluoric acid the effects of bombardment were still evident. There was, however, considerahle reduction in the tolerable reverse voltage. There is nothing in our experience to date to suggest that hombarded surfaces treated in accordance with the simple straightforward methods outlined above, are in any wise temporary in character.

CONCLUSIONS

The experiments reported above have shown that rather pronounced changes in the electrical properties of silicon may be produced merely by bombarding the polished surface with positive ions. The ratio of forward to reverse currents, for example, which for the usual untreated silicon is seldom more than a few hundred, can be made more than 10,000. Experiments show that the effect depends to some extent on the type of ion gas used, helium being a preferred medium. The effect depends also on the velocity of the bombarding particles, the total bombarding charge and to a lesser extent on the temperature of the specimen during bombardment. Good results are obtained from bombarding potentials of 30 kv with current densities of 5 microamperes per square centimeter for periods of one or two minutes. The temperature should preferable be about 300°C.

Ordinarily the properties of silicon are materially affected by impurity

content. In the case of bombarded silicon the effect is much less. More particularly it is possible to contaminate silicon with impurities such as boron to the point where its rectifying properties are almost completely lost and by bombardment it is possible to convert the crystal into a very useful rectifier. It is possible to produce results similar to the above by exposing the crystal to radioactive polonium. Bombarded materials appear to be relatively stable.

The writer wishes to express his appreciation of the encouragement and help of Dr. G. C. Southworth in the preparation of this paper, to A. J. Mohr, Jr., for his able assistance in the experimental work, and to numerous associates in Bell Telephone Laboratories for their assistance in preparing materials and in making special tests for which the author was not adequately equipped.